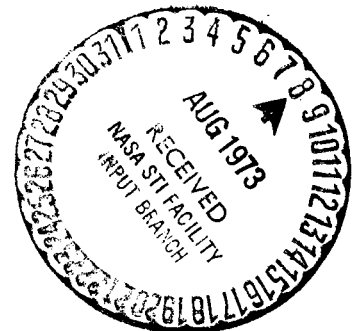P A
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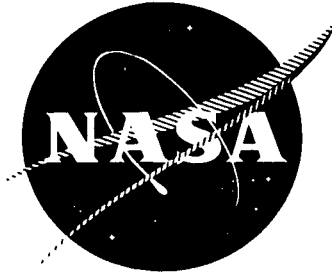
DEVELOPMENT OF LARGE DIAMETER
CARBON MONOFILAMENT

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16. Abstract

A process for preparing large-diameter carbon-boron monofilament was developed. The process involves chemical vapor depositing a carbon-boron alloy monofilament from a BCl_3, CH_4, and H_2 gas mixture onto a carbon substrate.

Amorphous alloys were formed when gaseous mixtures containing greater than 20 percent methane (80 percent BCl_3) were used. The longest uninterrupted lengths of carbon-boron monofilament were produced using a CH_4/BCl_3 gas ratio of 2.34. It was found that the properties of the carbon-boron alloy monofilament improved when the carbon substrate was precleaned in chlorine.

The highest strength monofilament was attained when a CH_4/BCl_3 gas volume ratio of 0.44 was used. The average strength of one run was over 345 kN/cm^2 (500 ksi), and the modulus was over 28×10^6 N/cm^2 (40×10^6 psi). While the highest strengths were attained in this run, the 0.44 gas ratio and other CH_4/BCl_3 ratios less than 2.34 would not yield long runs. Runs using these ratios were usually terminated because of a break in the monofilament within the reactor.

It is felt that better process control could probably be achieved by varying the amount of hydrogen; the BCl_3/H_2 ratio was kept constant in these studies.

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SUMMARY

The purpose of this work was to develop a process for preparing large-diameter carbon monofilament. The process selected involved chemical vapor deposition using boron trichloride, methane and hydrogen gases and a conventional boron type reaction in which the substrate is resistively heated.

Amorphous carbon-boron alloys were formed when gas mixtures containing greater than 20 percent methane (80 percent BCl_3) were used. The strongest carbon-boron monofilament was achieved using a CH_4/BCl_3 gas ratio of 0.44. This gas ratio produced a monofilament in which the average composition of the deposit was 75 w/o boron and 25 w/o carbon. When this high an amount of boron is attained, it is suspected that the deposit reacts more readily with the impurities present on the surface of the carbon substrate.

The carbon-substrate fiber was precleaned in chlorine and used as a substrate. With the precleaned substrate, the strength of the carbon-boron alloy monofilament was considerably improved.

The experimentation showed that high strength, high modulus carbon-boron alloy monofilament can be produced from a BCl_3, CH_4, and H_2 gas system. The modulus of the monofilament appears to be linearly dependent upon the percent of boron in the monofilament.

Neither the mechanical properties of the monofilament at elevated temperature nor the mechanical properties of composites fabricated using this monofilament were determined in this investigation.

In these investigations, the BCl_3/H_2 ratio was held constant while the BCl_3/CH_4 ratio was varied. It is felt that better process control could be achieved by varying the CH_4/H_2 ratio while maintaining a constant BCl_3/CH_4 ratio.

INTRODUCTION

The object of this program was to optimize the UARL chemical vapor deposition process to produce a large-diameter, high-strength, high-modulus carbon monofilament. Parameters such as deposition temperature, substrate velocity, reactor geometry, gas ratios and total reactant gas flows were studied. The effect of variations of these parameters were noted from both property measurements such as diameter, tensile strength, Young's Modulus and density, and from the optical and electron microprobe analyses.

The program was divided into the four tasks listed:

Task I   -   Process Development and Optimization

Task II   -   Property Evaluation

Task III   -   Reports

Task IV   -   Monofilament Production and Delivery

BACKGROUND

There has been a great deal of interest recently in the development of carbon reinforcement for metal matrix applications. Most of this effort has been directed toward the use of carbon multifiber yarns and tows. Carbon yarns are becoming more readily available with various strengths and moduli and the cost of these yarns is being reduced continuously. Initially attempts were made to produce these yarns with high moduli, but recently attention has been given specifically to developing a low cost carbon yarn with little scatter in strength and modulus. As the price of these yarns has been lowered, the incentive for using carbon yarn in all types of composites has increased. Adding to the impetus to use this yarn was the fact that carbon researchers have even reported an increase in strength of carbon at elevated temperatures. The low cost of carbon yarn made it attractive for use in aluminum and its high temperature properties has induced researchers to consider it for use in high temperature matrices such as nickel.

For the past several years there has been a great deal of effort directed toward producing carbon-aluminum and carbon-nickel composites. With any metal matrix one of the most difficult problems has been to impregnate the yarn with metal matrices so that the individual fibers in the yarn would be evenly dispersed. There is also an additional problem that the fibers are easily deteriorated by reactions with the matrix material. If attempts are made to coat the fibers with barrier layers care has to be taken that the small carbon fibers are not affected by diffusion of the coating into the body of the fiber.

Although some success has been obtained in forming carbon yarn-aluminum composites (Ref. 1), these composites still do not have properties competitive with those of boron-aluminum composites containing relatively large boron filaments.

The relative advantages and disadvantages of using carbon multifiber yarns and tows versus using carbon monofilaments have been discussed in Ref. 2. Fabrication problems would be greatly reduced when large diameter carbon monofilaments are used. Composite fabrication techniques currently used with boron filaments could be transferrable and the broad background of boron-aluminum composite experience could be utilized, instead of being forced to develop a whole new technology based upon small diameter carbon multifiber yarns and tows. In addition, protective coatings could be applied much more easily on large diameter monofilaments. Also, the relative fraction of coating material to filament area would be much less for the monofilaments, thus increasing the effective volume fraction of usable reinforcement and lessening the effect of the coating on the properties of the composite.

In an effort to obtain large diameter carbon monofilament for use as reinforcement for metal matrix composites, NASA-Lewis awarded several contracts to develop large diameter carbon monofilaments using different fabrication methods. The first method involved the impregnation with resin of commercially available small-diameter carbon yarns and tows. The resin impregnated bundles was then pyrolyzed to form a carbon yarn-carbon matrix composite monofilament (Refs. 3 and 4). Although reasonable strengths were obtained, difficulty was encountered in making these composite filaments because of nonuniform impregnation and cracking due to thermal expansion mismatches during pyrolysis.

The second approach consisted of using the chemical vapor deposition (CVD) method. Contracts were awarded to Hough Laboratory (Refs. 5 and 6). Initial work was done using a tungsten wire substrate, but it was found that better results were obtained using a carbon fiber substrate. Initially, pure pyrolytic graphite was deposited upon the substrate, but it was found that failure would occur by telescoping of the carbon layers over each other. This problem was elimianted by the addition of borane gas to the reactant hydrogen-hydrocarbon gases, which caused boron to be deposited to pin the carbon slip planes. This material contained approximately 30-40 percent boron.

UARL also has done research in the area of large-diameter carbon-base monofilaments. Attempts have been made using resin pyrolysis, direct conversion of large organic precursor fibers and the CVD process. Each technique had drawbacks, but the CVD process was selected for further study because it was felt to have the most potential for making the desired monofilament, even though the monofilaments produced were initially weak. It was decided to employ a combination of methane and boron trichloride as the reactant gases. The reactor used was similar to that used for boron filament development, Fig. 1, where the substrate is heated resistively and is drawn through mercury seals into a chamber where the reactant gases are introduced. Carbon fiber produced by Great Lakes Carbon Company was chosen as the substrate because of its low density and because of previous experience.

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Previous to this contract, a cursory investigation was conducted to determine what amounts of boron addition would be particularly suitable for producing high quality carbon monofilament. Gases were used with compositions of 4%, 8%, 9%, 15%, 23%, 40%, 72%, 83%, 88% and 92% methane with BCl_3; hydrogen was also added. The strengths of the monofilament produced are presented in Fig. 2. The higher strength monofilaments appeared to be produced in two compositional regions, one produced from a gas containing 8% CH_4, the other containing 72% CH_4. X-ray investigations indicated that the boron carbide (B_4C) pattern was strongest in monofilament produced from gases with 8% CH_4 while the monofilament produced from gases with higher percentages of CH_4 appeared to be amorphous. The monofilament thus produced was a carbon-boron alloy. It was felt that it was in this compositional region that the kind of monofilaments desired would be attained. At this point the best monofilament had an overall composition of about 50% carbon and had a strength of nearly 206 kN/cm^2 (300 ksi) and a modulus of 28 kN/cm^2 (40 x 10^6 psi). Unfortunately monofilament of even this quality could not be produced consistently. As a consequence, a program was outlined to explore various compositions further while also trying to optimize the other processing parameters.

CONTRACT EXPERIMENTAL PROGRAM

In initial experiments, using the information attained in the preliminary study, the parameters were set up for investigations. These are presented in Table I. Temperatures from 1125°C to 1205°C, drawing rates of 0.338 to 0.507 cm/sec and methane to boron trichloride ratios from 0.44 to 10.1 (Y_1 to Y_5) were employed in a 58 cm reactor. The BCl_3/H_2 ratio was held at 1.0 and the total flow rates of 380 cc/min, 760 cc/min and 1520 cc/min were used. At a total gas flow of 1520 cc/min monofilament production could not be satisfactorily maintained, so this flow was not investigated further.

Data from these initial experiments are presented in Table II. As can be seen, the data are inconsistent. Diameters did not vary as would be expected by varying substrate velocity, and, at a fixed gas ratio and process temperature, the scatter in the average ultimate tensile strength is excessive. For these reasons, it was suspected that there was some factor which was masking the effect of the processing parameters on the monofilament strength. A prime suspect was the substrate fiber which varied in diameter and resistance due to impurities and other factors.

Surface Observations

Further insight into this problem was obtained by examining the surfaces of high quality carbon-boron monofilament, as well as some of the lower strength monofilaments by means of a light microscope. Figures 3 and 4 show photomicrographs of the surfaces of monofilaments. Examination of these surfaces indicated that the uniform small kernels were typical of the higher strength monofilaments and the

large kernels were commonly observed in low strength monofilaments with considerable scatter in their strength. Since it can be assumed that the outgrowths observed are caused by surface imperfections the approach taken of cleaning the substrate before carbon alloy deposition appeared to be a logical one. In addition, the uniformity of the kernels in higher strength fibers also indicates that good process controls are essential for producing high quality fiber.

Cleaning of the Substrate

Sections of carbon-boron alloy monofilament containing flaws and a randomly selected section of as-received carbon substrate fiber were chemically analyzed with an electron microprobe. The impurities found in the flaws of the carbon-boron alloy monofilament were Ca, K, Fe, S, Si, and Al. One flaw and the impurity associated with it is shown in Figure 5.

The impurities found on the surface of the as-received carbon substrate were Ca, K, Fe, S, Si, and Ni. Figure 6 shows a section of this fiber and the impurities associated with it.

Many attempts were made to clean the carbon substrate fiber. It was separately passed through ultrasonically agitated solutions of acids, commercial bleach, acetone, carbon tetrachloride, alcohol, and water. Two hot filament experiments were also conducted. They were: 1) passing the fiber through a reactor at a temperature of 1400°C under H_2 and, 2) passing the fiber through a reactor at a temperature of 1450°C under BCl_3. None of these methods adequately cleaned the surface of the fiber. Monofilament made from the "precleaned" substrate fiber was comparable in strength and surface appearance to monofilament made previously.

Next, the carbon fiber substrate was given the following treatments. The chlorine cleaning was done in an RF reactor.

Sample

1	Cleaned in chlorine at 1550°C
2	Cleaned in argon at 1800°C
3	Cleaned in chlorine at 1650°C with a further cleaning in hydrogen at 1560°C
4	Cleaned in chlorine at 1650°C and coated with carbon at 1580°C
5	Cleaned in chlorine at 1650°C and coated with carbon at 1600°C
6	Cleaned in chlorine at 1650°C

The results of the spectral scan analysis are given in Table III. These data show that all of the samples contain sulfur even after treatment of the substrate. The sulfur appears to be an integral part of the carbon substrate fiber which may or may not affect the carbon-boron alloy monofilament properties. The other impurities also could not be removed by heating the substrate in chlorine at 1550°C or by heating it in argon at 1800°C as can be seen from the results from samples 1 and 2. However, by raising the chlorine treatment temperature to 1650°C the impurities, except for sulfur, were cleaned from the monofilament. In sample 3, a hydrogen post treatment also was given to the fiber, but it is not clear that it is necessary. Samples 4 and 5 were coated with carbon in an attempt to prevent sulfur from interacting with the carbon-boron alloy during deposition, although it should be noted that sulfur has not been detected at any flaw or fracture site in the carbon-boron alloy monofilament. Fracture studies of carbon-boron alloy monofilament produced from a carbon coated substrate showed that the coating carbon appeared to introduce fracture sites either at the carbon-boron alloy-coating carbon interface or at the coating carbon-carbon substrate fiber interface. All tensile fractures of monofilament produced from carbon coated substrate fiber exhibited substrate fiber pullout and since the average tensile strengths of all runs of monofilament produced with a carbon coated substrate fiber centered around 104 kN/cm^2 (150 ksi), the coating was no longer used. Sample 6 cleaned only in chlorine at 1650°C and data in Table III and Figures 7 and 8 indicate that this was adequate to remove all the impurities except sulfur for this shipment of carbon substrate fiber. The flaw shown on the as-received substrate fiber in Fig. 7, is similar to the flaw shown in Fig. 6 and is an example of the worst flaw found on the fiber. The frequency of occurrence of this type of flaw varies from shipment to shipment. When a substrate having 8 to 9 of these flaws per meter (approximately 3 per foot) is cleaned in chlorine and examined, the flaws are no longer apparent. It is reasonable to assume that the impurity or impurities associated with this type of flaw reacted with Cl_2 to form a chloride and subsequently evaporated .

The photograph of the carbon substrate fiber cleaned in Cl_2 at 1650°C (Fig. 7) shows some pitting. Chlorine cleaning experiments conducted after the cleaning of the fiber shown in Fig. 7 and discussed below have shown that each lot number of carbon substrate fiber and even separate spools from the same lot may require different cleaning parameters. In retrospect, it is felt that the Cl_2 cleaned fiber shown in Fig. 7 was overcleaned and slightly etched.

The substrate fiber cleaned in chlorine at 1650°C was used to make carbon-boron alloy monofilament and the data are presented in Table IV.

The results of this study were quite promising, in that the strengths of the fibers produced on a clean substrate were quite similar. Although they were not as high as the best fiber produced, they did give some indication that consistency can be obtained with better process controls.

Comparison of Monofilament Produced from Different Substrates and Monofilament Composition Studies

Monofilament was then made using a new spool of as-received carbon substrate fiber labeled by Great Lakes Carbon Company as Lot #1115. This spool was part of a shipment received the latter part of August. Various parameters were run and the parameters which yielded strong fibers were repeated. The data for these experiments are given in Table V.

These monofilaments obtained using a gas ratio γ_1, were the highest strength ones produced to this point and indicated the potential of this BCl_3/CH_2 process for forming high quality fiber. The best run produced monofilament with an average strength of over 344 kN/cm^2 (500 ksi) and the individual strengths of over 462 kN/cm^2 (670 ksi). It was easily handleable, could be bent in a small radius and compared favorably with the best boron on tungsten fiber formed experimentally or in production. Unfortunately, these studies also showed that the parameters had not been well enough controlled to permit this type of high quality carbon alloy fiber to be formed reproducibly.

Since the highest strength monofilaments were obtained with CH_4/BCl_3 gas ratio of 0.44 (γ_1) with an uncleaned substrate, the next logical step was to clean the new carbon substrate which yielded the high strength monofilament and repeat the experiments. The cleaning process of 1650°C in chlorine was used because it had sufficiently cleaned the previous substrates. Unfortunately, as can be seen from the data in Table VI, monofilament with very poor properties were obtained. The appearance of the monofilament indicated that the substrate had not been thoroughly cleaned. It was at this point that it was realized that the time and temperature of the cleaning process might be quite critical, differing for various substrates, and should be investigated in detail. Because of time limitations, the cleaing temperature for the substrate was simply raised to 1720°C and fortunately considerable improvement in the properties of the carbon alloy monofilament was attained. See Table VII. The fact that the strength of the fiber was not as high as had been obtained previously was not too surprising as runs with this gas composition were difficult to control.

When gas ratio γ_1 was used, only short runs of carbon-boron alloy monofilament were attained. The runs were usually terminated by monofilament breaks within the reactor during disposition. These breaks were observed with a light microscope and breaks from two separate runs are shown in Fig. 9. The breaks are apparently caused by melted regions on the monofilaments. Assuming that these melts are low melting temperature B-X eutectics, it would follow that the greater the percent of boron in the deposit, the greater the chance of forming a eutectic. In many experiments, carbon-boron monofilament could not be produced using gas ratio γ_1 because breaks occurred shortly after the substrate fiber had been heated to the deposition temperature. Yet, when the gas ratio was changed to γ_2, using the same substrate fiber, long runs of average quality monofilament could be produced.

Also, it was felt that the amount of hydrogen used in the gas mixture was a major factor in determining the percent of boron present in the deposit. From the reactions given below

$$CH_4 \longrightarrow C + 2H_2$$

$$2BCl_3 + 3H_2 \longrightarrow 2B + 6HCl$$
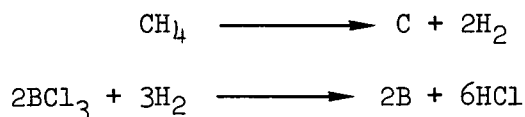
it would be expected that increasing the hydrogen gas in the mixture would decrease the carbon content of the fiber and increase the boron content, while decreasing the hydrogen would have the opposite effect.

With these considerations in mind, a gas ratio was conceived that would yield a carbon-boron alloy monofilament in which the percent of boron in the deposit would be between that obtained from gas ratio Y_1 and Y_2. The gas ratios for this new composition were $CH_4/BCl_3 = 1.77$, $CH_4:H_2 = 1.8$ and $BCl_3/H_2 = 1$, and was designated by the CH_4/BCl_3 gas ratio of 1.77.

To investigate the effect of H_2 on the composition of the monofilament another gas composition with the same CH_4/BCl_3 ratio, 1.77, but containing less hydrogen was established. This composition was designated 1.77'and the gas ratios were $CH_4/BCl_3 = 1.77$, $CH_4/H_2 = 4.2$ and $BCl_3/H_2 = 2.4$.

Carbon-boron alloy monofilament was produced using these new gas ratios and Y_2. The substrate fiber used was Lot #1115 cleaned in Cl_2 at 1720°C. The data for the monofilament produced using gas ratios 1.77 and Y_2 are shown in Table VIII and the data comparing monofilament produced using gas ratios 1.77 and 1.77' are shown in Table IX.

Concurrent with the above experimentation, further experiments were conducted with gas ratio Y_2. This ratio was chosen to produce fiber to satisfy Task IV of the contract – shipment of monofilament to NASA, and the experiments were made to optimize the strength of the monofilament while satisfying diameter requirements. Data from the experiments are shown in Table X.

The final experimentation under the contract was a series of runs to investigate the composition of the carbon-boron alloy monofilament and the modulus for that composition. Monofilament, produced from CH_4/BCl_3 ratios of 0.44 (Y_1), 1.77, and 2.34 (Y_2) were chosen for study. The properties and compositions are given in Table XI. The average weight percent boron in the deposit varied from 67 for Y_2 to 75 for Y_1 while the modulus varied from 26×10^6 kN/cm^2 (37×10^6 psi) to 33×10^6 kN/cm^2 (49×10^6 psi). Unfortunately, time did not permit these studies to be done with a chlorine cleaned substrate fiber.

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A plot of the modulus of carbon-boron alloy monofilament as a function of w/o boron of the monofilament is given in Fig. 10. The end points of the abscissa are the average modulus of the carbon substrate fiber at 0 w/o boron and boron fiber at 100 w/o boron.

The density of monofilament from run numbers N232, 59 w/o B, N262, 65 w/o B and N266, 75 w/o B was measured by Dynatech R/D Company of Cambridge, Massachusetts. These data are shown in Table XII.

DISCUSSION

The data in Table IX shows the influence of H_2 in the H_2, BCl_3, CH_4 system. These data and the data in Table XI indicate the control of the monofilament composition available by varying the gas mixture. Data in Table XI show that the monofilament composition was not sensitive to deposition temperature over the range studied. Note the data from run N261 deposited at temperature T_1 and run N263 deposited at temperature T_3.

Gas ratio 1.77 did not produce monofilament that was radically different in w/o boron from ratio Y_2. The data in Table VIII (results of a series of experiments investigating monofilament strength as a function of temperature for gas composition 1.77 and Y_2) show a trend toward higher strength as the deposition temperature is increased. Run N238, produced using a gas ratio of 1.77 and deposition temperature of T_4 (1205°C) is exceptionally strong. Chemical analysis of this monofilament was not completed within the contract period and the reason for the anomalous diameter is not known. Cross sections of high strength monofilament showed that a fairly uniform coating of boron-carbon alloy was deposited. X-ray diffraction studies indicated that they consisted of amorphous type material.

Cross sections of monofilament produced using higher CH_4/BCl_3 gas ratios were somewhat different in that they tended to form zones of different composition during the deposition process. In early experimentation, monofilament was produced using a gas ratio Y_3 or 83% methane. The ratio of CH_4 to H_2 in gas composition Y_3 is 5 to 1 as compared with 2.34 to 1 for gas composition Y_2. As discussed, the higher CH_4 to H_2 ratios enhances the deposition of carbon. In these experiments, the reactor clouded over and monofilament temperature could not be accurately measured. Figure 11 shows a monofilament produced from gas composition Y_3 with 246 watts applied. Note that the monofilament is starting to form zones which become more pronounced as the power to the monofilament is increased. See Fig. 12 with 264 watts applied and Fig. 13 with 300 watts applied to the monofilament. Similar results were obtained for monofilaments produced using other gas compositions with $CH_4:H_2$ ratios greater than 2.34. In each case the amount of C in the fiber increases and the tendency to form zones also increased. The reason for the multiple zones cannot be explained at this time.

The data in Table VIII and X were used to select conditions for producing mono-filament to ship to NASA. The parameters were gas ratio γ_2, Draw Speed 0.253 cm/sec (30 ft/hr) and a deposition temperature of 1185°C. Continuous lengths of 73 meters (240 ft) and 89 meters (292 ft) with average tensile strengths of 254 kN/cm^2 (369 ksi) and 261 kN/cm^2 (379 ksi) were shipped.

CONCLUSIONS

High modulus carbon-boron alloy monofilament can be chemically vapor deposited onto a carbon substrate fiber from a H_2, BCl_3 and CH_4 gas system. Modulus is linearly dependent on the w/o boron in the monofilament. Monofilaments with composition 59 w/o boron through 75 w/o boron were amorphous. The w/o boron on the monofilament was controlled by the gas mixture and was relatively insensitive to deposition temperature over the range studied.

Studies have shown that high strength monofilament can be produced. However, as yet the parameters for forming this monofilament have not been defined. It is known that the condition of the substrate fiber is important in determining the strength of the monofilament, but the gas ratios, temperature and drawing rate must be studied further to optimize the monofilament producing process.

SUGGESTIONS FOR FUTURE WORK

The object of any future work should be to optimize the strength of a monofila-ment using a fixed gas ratio. Optimization of the strength would be accomplished by continued experiments on cleaning the substrate fiber, experiments to determine the best total gas flow and deposition temperature and experiments with reactor geometry (from experience with boron fiber technology, it is known that improvements in deposition can be achieved by control of gas flows and composition at various points along the fiber in the reactor). In addition, it would be meaningful to compare monofilaments produced in a direct current reactor (substrate is resistively heated through mercury contacts) with that produced in a radio frequency reactor (substrate is heated by electro-magnetic coupling to a radio frequency source) to determine which method yields the best results.

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Table I

Parameter Designation

Temperature

Symbol	T_1	T_2	T_3	T_4
Value °C	1125	1150	1175	1205

Substrate Velocity

Symbol	β_1	β_2	β_3
Value cm/sec (ft/hr)	0.338 (40)	0.423 (50)	0.507 (60)

CH_4/BCl_3 Ratio

Symbol	γ_1	γ_{1a}	γ_2	γ_3	γ_4	γ_5
Value	0.44	0.89	2.34	4.98	8.07	10.14

Total Gas Flow

Symbol	X_1	X_2	X_3
Value cc/min	380	760	1520

Table II - Results of Initial Deposition Experiments

Parameters	Run No.	Diameter μ(mils)		Avg uts KN/cm^2	ksi	Parameters	Run No.	Diameter μ(mils)		Avg uts KN/cm^2	ksi
γ_2 T_3 β_1	N 65	76.2	3.0	137	199	γ_2 T_3 β_1	N 3	88.9	3.5	124	180
β_2	N 68	73.7	2.9	152	220	β_2	N 6	83.8	3.3	143	208
β_3	N 71	71.1	2.8	131	190	β_3	N 9	78.7	3.1	125	181
γ_3 T_3 β_1	N 80	76.2	3.0	111	161	γ_3 T_3 β_1	N 12	88.9	3.5	79	114
β_2	N 83	78.7	3.1	76	110	β_2	N 15	88.9	3.5	59	86
β_3	N 86	63.5	2.5	120	174	β_3	N 18	86.4	3.4	41	60
γ_4 T_3 β_1	N 89	66.0	2.6	65	94	γ_4 T_3 β_1	N 40	73.7	2.9	101	146
β_2	N 92	68.6	2.7	47	68	β_2	N 43	83.8	3.3	48	70
β_3	N 95	76.2	3.0	43	63	β_3	N 46	86.4	3.4	44	64
γ_5 T_3 β_1	N 98	76.2	3.0	37	54	γ_5 T_3 β_1	N 49	88.9	3.5	65	94
β_2	N101	71.1	2.8	39	56	β_2	N 52	71.1	2.8	57	85
β_3	N104	66.0	2.6	59	86	β_3	N 55	71.1	2.8	23	33

Table III

Electron Microprobe Spectral Scan
Analyses of Cleaned Substrate Fiber

Sample	Cleaning Procedure	Elements Detected		
		Major	Minor	Trace
1	Cl_2 1550°C	S,Fe,Cr,Cl	Ni	---
2	Ar 1800°C	S	---	Fe,Si,Mn
3	Cl_2 1650°C and H_2 1650°C	S	Cl	---
4	Cl_2 1650°C Carbon Deposit at 1580°C	S	---	---
5	Cl_2 1650°C Carbon Deposit at 1600°C	S	---	---
6	Cl_2 1650°C	S	---	---

Table IV

Individual Tensile Tests
(Substrate Precleaned in Cl_2 at 1650°C)
Gage Length = 2.54 cm (1 in.)

Run No. Parameter	N-152 $\gamma_2\,\beta_1 T_3$	N-153 $\gamma_{1a}\beta_1 T_1$	N-157 $\gamma_{1a}\beta_1 T_1$
Diameter (μ) (mils)	63.5 (2.5)	59.7 (2.35)	61.0 (2.4)
UTS (10^3) (N/cm^2) (psi)	106 (153)	143 (207)	107 (155)
	135 (196)	151 (219)	137 (199)
	141 (204)	151 (219)	145 (210)
	176 (255)	151 (219)	160 (232)
	176 (255)	175 (253)	191 (277)
	190 (275)	175 (253)	199 (288)
	218 (316)	183 (265)	206 (299)
	218 (316)	210 (305)	214 (310)
	239 (346)	215 (311)	229 (332)
	246 (356)	223 (323)	244 (354)
Avg. UTS (10^3) (N/cm^2) (psi)	184 (267)	177 (257)	183 (265)
Std. Dev. UTS (10^3) (N/cm^2) (psi)	47 (68)	30 (43)	44 (64)
Coeff. of Var. (%)	25	17	24

Table V-A

Individual Tensile Tests (SI Units)
(As-received Substrate Lot No. 1115)
Gage Length = 2.54 cm (1 in.)

Parameters	$\gamma_2\beta_1T_1$		$\gamma_2\beta_1T_2$	$\gamma_2\beta_1T_3$		$\gamma_1\beta_1T_1$						$\gamma_1\beta_1T_2$		
Run Nos.	N-163	N-168	N-169	N-164	N-170	N-165	N-167	N-171	N-173	N-174	N-190	N-166	N-176	N-191
Diameter (μ)	53.3	63.5	63.5	63.5	68.6	45.7	66.0	66.0	63.5	66.0	63.5	71.1	78.7	71.1
UTS(N/cm^2 x 10^3)	60	92	63	28	108	95	273	143	70	59	81	163	96	95
	74	92	77	56	121	136	313	178	99	85	108	179	142	99
	74	99	110	91	121	150	314	182	106	91	119	202	146	109
	83	106	123	91	127	190	345	208	119	104	126	264	210	129
	92	131	141	99	139	244	358	224	137	144	133	308	210	135
	132	145	162	126	159	258	362	228	141	163	133	355	215	137
	159	162	197	130	213	271	371	243	183	163	133	371	219	140
	164	178	201	148	217	326	383	246	186	189	141	373	233	146
	179	197	211	161	224	408	391	266	197	189	155	409	275	166
	219	204	235	186	235	408	464	286	232	215	173	415	403	197
Avg. UTS	124	141	152	112	166	249	357	220	147	140	130	304	215	135
Std. Dev.	55	43	59	48	50	109	52	43	51	52	25	96	84	30
Coeff. of Var. (%)	44	31	39	43	30	44	15	20	35	38	19	32	39	23

Table V-B

Individual Tensile Tests (English Units)
(As-received Substrate   Lot No. 1115)
Gage Length = 2.54 cm (1 in.)

Parameters	$\gamma_2 \beta_1 T_1$		$\gamma_2 \beta_1 T_1$	$\gamma_2 \beta_1 T_3$		$\gamma_1 \beta_1 T_1$						$\gamma_1 \beta_1 T_2$		
Run Nos.	N-163	N-168	N-169	N-164	N-170	N-165	N-167	N-171	N-173	N-174	N-190	N-166	N-172	N-191
Diameter (mil)	2.1	2.5	2.5	2.5	2.7	1.8	2.6	2.6	2.5	2.6	2.5	2.8	3.1	2.8
UTS (ksi)	87	133	92	41	157	138	396	207	102	85	118	236	139	138
	107	133	112	81	175	197	453	258	143	123	157	260	206	143
	107	143	159	132	175	217	455	264	153	132	173	293	212	158
	121	153	178	132	184	276	500	301	173	151	183	382	305	187
	133	190	204	143	201	354	519	325	199	208	193	447	305	195
	191	210	235	183	231	374	525	330	204	236	193	515	312	198
	231	235	286	188	309	393	538	352	265	236	193	537	318	203
	237	259	292	214	315	472	555	357	270	274	204	540	338	211
	260	286	306	234	325	591	566	386	286	274	224	593	398	241
	318	296	341	269	341	591	672	414	336	311	251	602	584	285
Avg. UTS	179	204	220	162	241	360	518	320	213	202	189	440	312	196
Std. Dev.	79	63	85	69	73	158	75	63	74	76	36	139	122	44
Coeff. of Var. (%)	44	31	39	43	30	44	15	20	35	38	19	32	39	23

Table VI

Individual Tensile Tests
Substrate Cleaned under Cl_2 at 1650°C
Gage Length = 2.54 cm. (1 in)

Run No.	N 209	N 210	N 211	N 212
Parameters	$\gamma_1\beta_1 T_1$	γ_1 0.254 cm/sec T_1	γ_1 0.254 cm/sec T_2	$\gamma_1\beta_2 T_2$
Diameters (μ) (mils)	66 2.6	66 2.6	71.1 2.8	66 2.6
UTS (10^3) (N/cm^2) (psi)	72 104	111 160	112 162	91 132
	84 123	130 189	112 162	117 170
	111 160	136 198	123 179	117 170
	111 160	150 217	123 179	124 179
	117 170	150 217	129 187	130 189
	117 170	169 245	134 195	130 189
	124 179	176 255	140 203	137 198
	130 189	182 264	151 219	137 198
	150 217	189 274	173 252	137 198
	176 255	221 321	185 268	150 217
Avg. UTS (10^3) (N/cm^2) (psi)	119 173	161 234	138 200	127 184
Std. Dev. UTS (10^3) (N/cm^2) (psi)	36 43	39 47	30 36	19 23
Coeff. of Var. (%)	25	20	18	13

Table VII

Individual Tensile Tests
Substrate Cleaned under Cl_2 at 1720°C
Gage Length = 2.54 cm (1 in.)

Run Nos.	N213		N214		N215	
Parameters	$\gamma_1 \beta_1 T_1$		$\gamma_1 \beta_1 T_2$		$\gamma_1 \beta_1 T_1$	
Diameter (μ) (mils)	63.5	2.5	66	2.6	68.6	2.7
UTS (10^3) (N/cm^2) (psi)	70	102	65	94	96	140
	189	275	104	151	181	262
	225	326	130	188	181	262
	225	336	143	207	217	315
	225	336	167	245	217	315
	225	336	208	301	229	332
	239	346	221	320	229	332
	239	346	221	320	241	350
	253	366	247	358	253	367
	253	366	272	395	253	367
Avg. UTS (10^3) (N/cm^2) (psi)	216	314	178	258	210	304
Std. Dev. UTS (10^3) (N/cm^2) (psi)	65	78	80	97	57	69
Coeff. of Var. (%)	25		36		23	

Table VIII

Individual Tensile Tests
Substrate cleaned under Cl_2 at 1720°C
Gage length = 2.54 cm. (1 in)

Run Nos. Parameters	N 220 $\frac{1}{2}\beta_1 T_1$		N 221 $\frac{1}{2}\beta_1 T_2$		N 222 $\frac{1}{2}\beta_1 T_3$		N 223 $1.77\,\beta_1 T_1$		N 224 $1.77\,\beta_1 T_2$		N 225 $1.77\,\beta_1 T_3$		N 238 $1.77\,\beta_1 T_4$	
Diameter (μ) (mils)	48.3	1.9	61	2.4	63.5	2.5	55.9	2.2	63.5	2.5	73.7	2.9	53.3	2.1
UTS (10^3) (N/cm^2) (psi)	73	105	114	166	169	245	18	26	77	112	99	145	101	147
	109	159	114	166	183	265	73	105	112	163	115	167	243	353
	134	194	145	210	183	265	105	153	141	204	167	242	293	426
	146	212	145	210	197	286	123	179	176	255	219	318	304	441
	158	229	152	221	211	306	127	184	218	316	219	318	334	485
	170	247	152	221	211	306	140	202	218	316	219	318	345	500
	170	247	168	243	225	326	154	224	218	316	224	326	345	500
	182	265	168	243	232	337	163	237	225	327	230	333	355	515
	207	300	175	254	232	337	172	250	232	336	230	333	355	515
	219	317	198	289	232	337	172	250	239	347	245	356	375	544
Avg. UTS (10^3) (N/cm^2) (psi)	157	227	153	222	207	301	125	181	186	269	197	286	305	443
Std. Dev. UTS (10^3) (N/cm^2) (psi)	53	64	31	38	28	34	59	71	68	82	62	75	98	118
Coeff. of Var. (%)	28		17		11		39		31		26		27	

Table IX

Strength and w/o Boron for Monofilament Produced
from Gas Ratios 1.77 and 1.77'
Substrate - GLRC Lot No. 1115 Cleaned in Cl_2 at 1720°C
Gage Length for UTS Data is 2.54 cm (1^{2}in.)

Run Nos.	N 232			N 224	
Parameters	1.77' β_1	T_2		1.77 β_1	T_2
Diameter (μ)(mils)	55.9	2.2		63.5	2.5
UTS (10^3) (N/cm^2) (psi)	91	132		77	112
	109	158		112	163
	127	184		141	204
	145	211		176	255
	163	237		218	316
	172	250		218	316
	172	250		218	316
	178	258		225	327
	181	263		232	336
	199	289		239	347
Avg. UTS (10^3) (N/cm^2) (psi)	153	223		186	269
Std Dev. (10^3) N/cm^2 (psi)	42	51		62	75
Coeff of Var. (%)	23			26	
Avg. w/o Boron	59			69	
Avg. Modulus (10^6) (N/cm^2) (psi)	20.7	30		No Data	
Std. Dev. (10^6) (N/cm^2) (psi)	2	3		No Data	

Table X

Individual Tensile Tests
Substrate cleaned under Cl_2 at 1720°C
Gage length = 2.54 cm (1 in.)

Run Nos.	N227		N230		N237		N242	
Parameters	$\frac{1}{2}\,\beta_1 T_3$		$\frac{1}{2}\,\beta_1\,T_4$		$\frac{1}{2}\,\beta_1\,T_4$		$\frac{1}{2}$ 30 ft/hr T_3	
Diameter (μ) (mils)	63.5	2.5	68.6	2.7	63.5	<2.5	63.5-81.3	2.5-3.2
UTS (10^3) (N/cm^2)(psi)	140	204	102	149	134	194	93	134
	168	244	199	288	145	210	98	143
	180	261	205	297	155	224	133	194
	180	261	211	306	176	255	140	204
	185	269	229	332	176	255	162	235
	194	281	241	350	180	261	197	285
	196	285	247	358	190	276	204	295
	206	299	247	358	211	276	204	295
	210	305			218	316	221	320
	210	305			225	327	260	377
	225	326						
	239	346						
Avg. UTS (10^3) (N/cm^2)(psi)	194	282	210	305	181	262	171	248
STD Dev. UTS (10^3) (N/cm^2)(psi)	32	38	57	69	37	45	66	79
Coeff. of Var. (%)	14		23		17		32	

TABLE XI

Strength, modulus and w/o boron for fiber produced from gas ratios γ_1, γ_2, and 1.77

Substrate - As received GLRC Lot 1115 Spool #2 Gage Length for UTS data is 2.54 cm (1 in.)

Run Nos.	N263		N265		N266		N264		N261		N262	
Parameters	$\gamma_1\beta_1 T_1$		γ_1 25 ft/hr 1080°C		γ_1 25 ft/hr 1105°C		1.77 $\beta_1 T_1$		$\gamma_2\beta_1 T_1$		$\gamma_2\beta_1 T_3$	
Diameters (μ) (mils)	58.4	2.3	59.7	2.35	63.5	2.5	53.3	2.1	53.3	2.1	63.5	2.5
UTS (10^3) (N/cm^2)(psi)	108	157	135	196	42	61	66	96	90	130	175	255
	125	181	135	196	63	92	76	110	100	145	182	265
	133	193	167	242	98	143	85	124	100	145	189	275
	149	217	183	265	161	234	95	138	110	159	196	285
	183	265	191	276	168	244	123	179	139	202	210	305
	216	313	198	288	181	263	142	207	159	231	218	316
	224	325	246	357	232	337	152	220	159	231	232	336
	232	337	254	369	239	346	161	234	179	260	232	336
	232	337	270	392	246	357	180	262	199	289	253	367
	257	373	349	507	256	371	180	262	219	318	260	377
Avg. UTS (10^3) (N/cm^2) (psi)	186	270	213	309	169	245	126	183	145	211	215	312
Std. Dev. (10^3) (N/cm^2) (psi)	65	78	81	97	94	113	52	63	55	66	35	42
Coeff. of Var.(%)	29		32		46		34		31		14	
Avg. Modulus (10^6) (N/cm^2) (psi)	33	49	32	46	33	48	27	39	26	37	28	40
Std. Dev. (10^6) (N/cm^2) (psi)	3	4	1	2	1	1	4	5	0.9	1	0.3	0.3
Avg. w/o Boron	75		75		75		70		68		67	
CH_4/BCl_3	0.44		0.44		0.44		1.77		2.34		2.34	

Table XII

Density of Monofilament With Various W/O Boron

Run No.	W/O Boron in Deposit	Density (g/cc)
N232	59	2.079
N262	65	2.188
N266	75	2.226

FIG. I

CHEMICAL VAPOR DEPOSITION REACTOR

SUBSTRATE FIBER SUPPLY SPOOL

GAS INLET

MERCURY ELECTORDE

REACTOR BODY

MERCURY ELECTRODE

GAS EXHAUST

TAKE UP MECHANISM

26

UTS VS MOLE % CH₄ FOR C (B) FIBER

CH₄, BCl₃, H₂ SYSTEM

FIG. 2

N—152   20μ

N—153   20μ

N—157   20μ

N—167   20μ

FIG. 3

FIG. 4
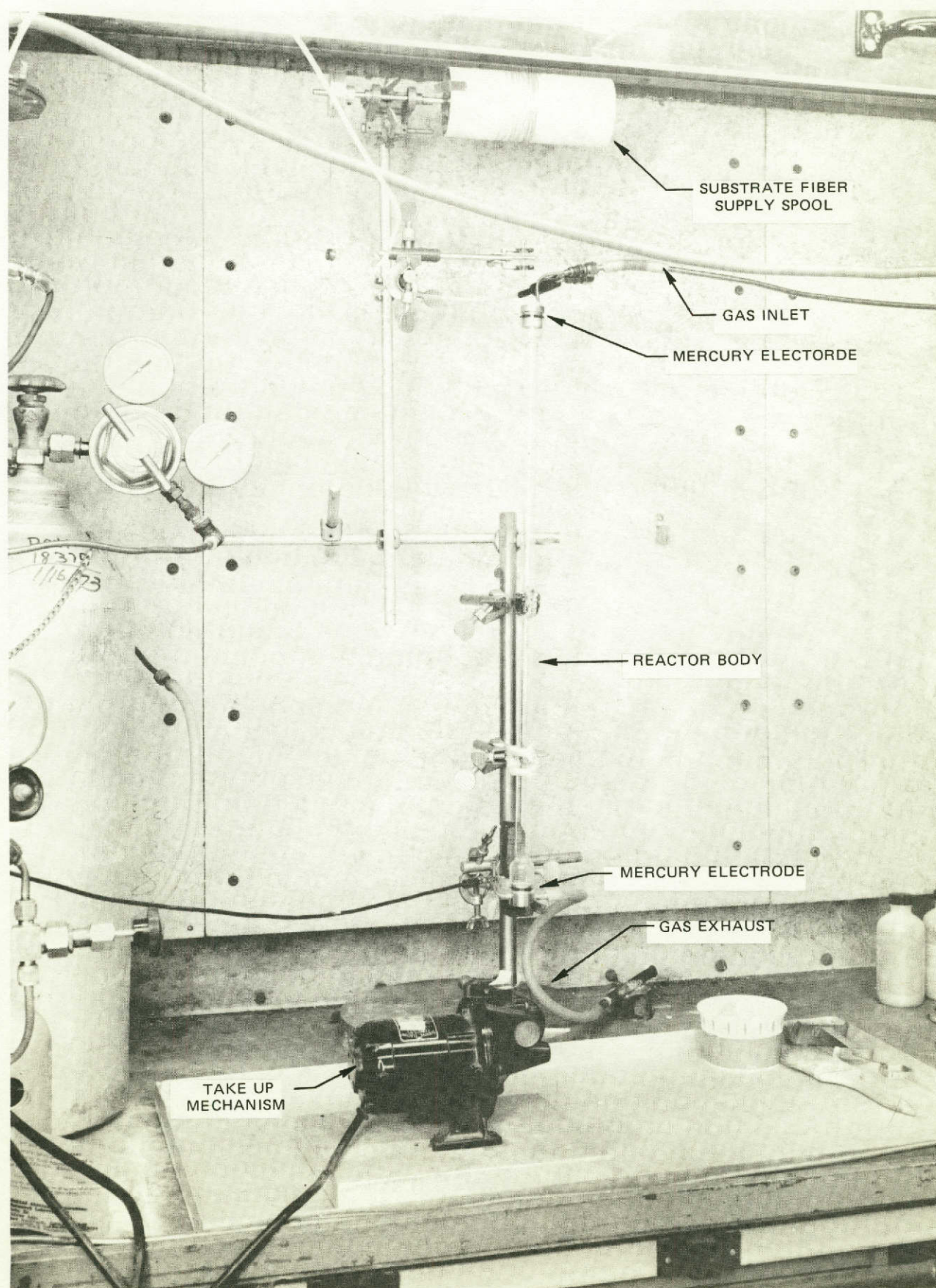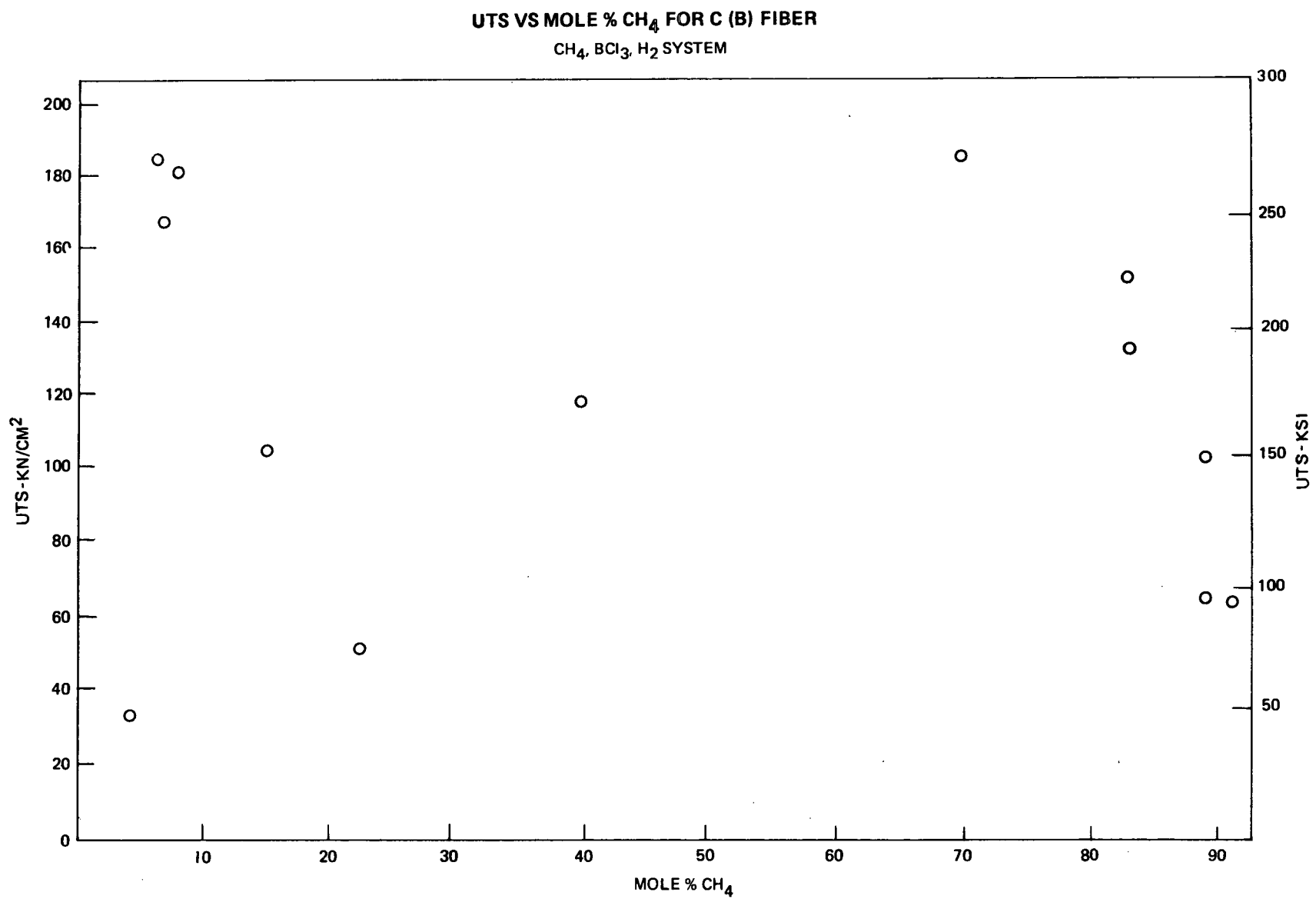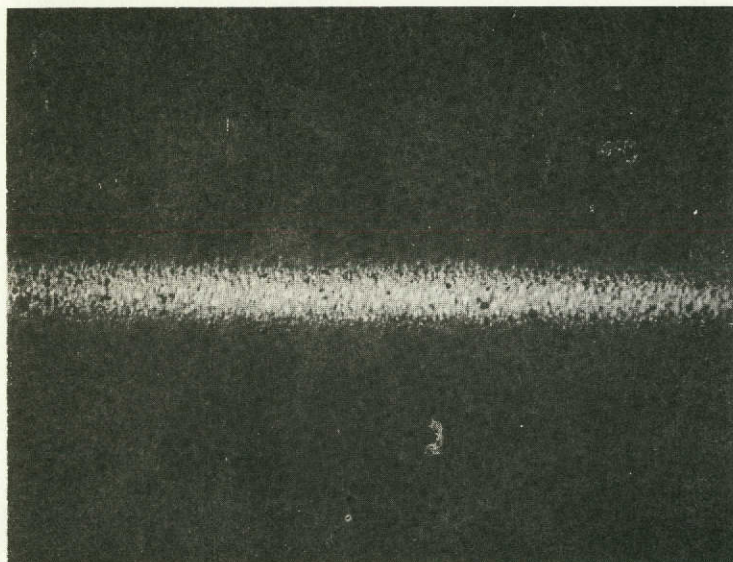
PHOTOGRAPHS OF SURFACE OF WEAK CARBON–BORON ALLOY
MONOFILAMENT

N 190   20μ

FIG. 5
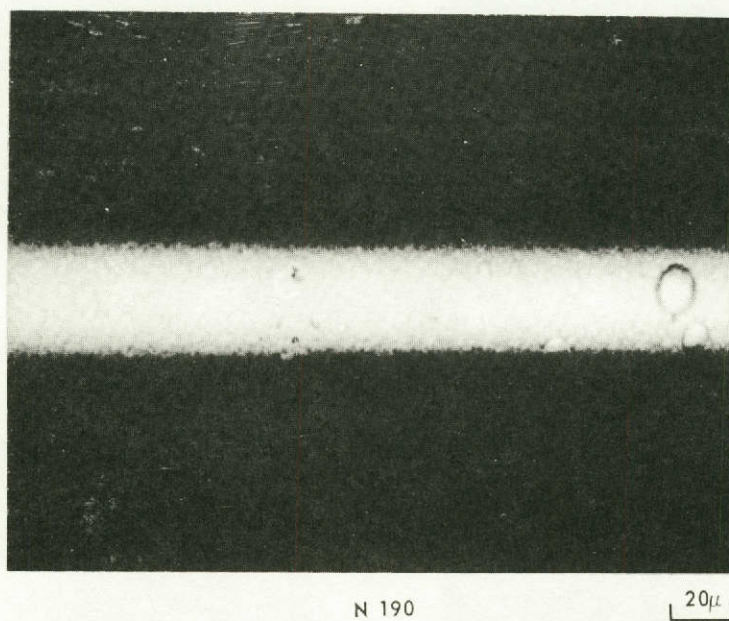
ELECTRON IMAGE AND DISTRIBUTION PHOTOGRAPHS OF A PORTION
OF THE BORON—CARBON ALLOY MONOFILAMENT SURFACE

ELECTRON IMAGE   20μ

CALCIUM X—RAYS
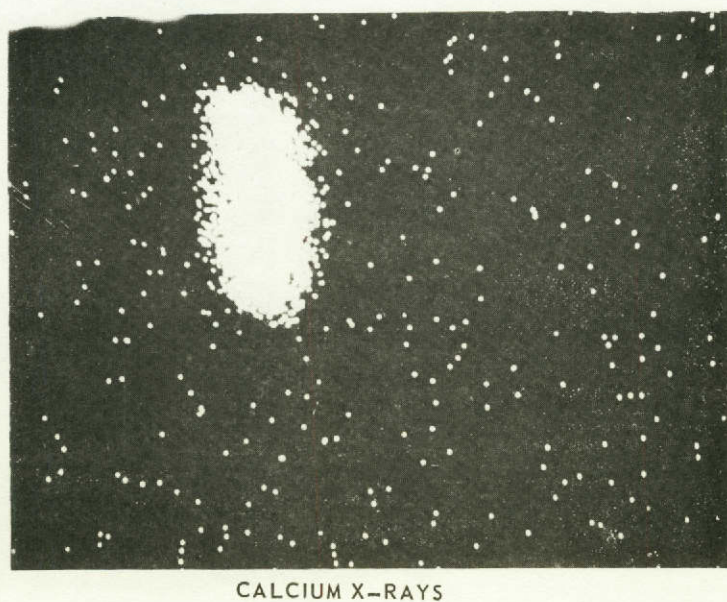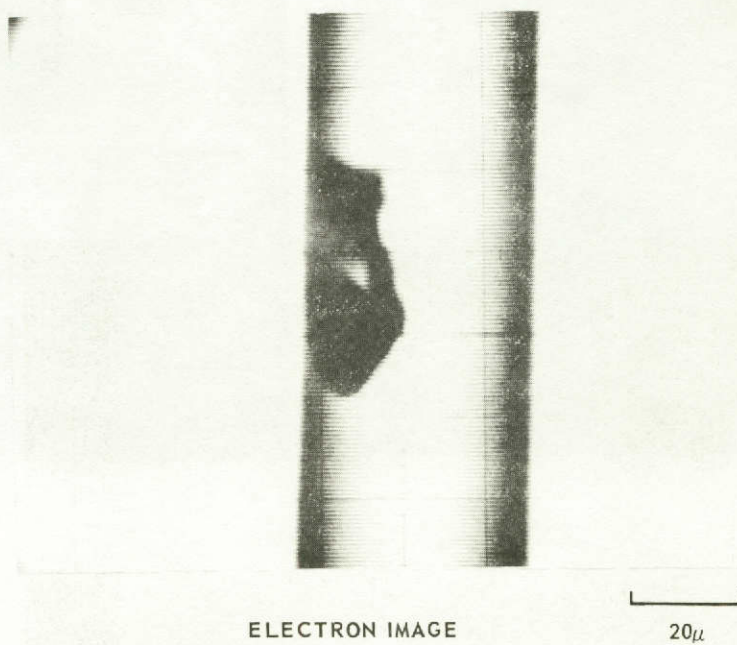
ELECTRON IMAGE AND X—RAY DISTRIBUTION PHOTOGRAPH OF A PORTION OF THE "AS RECEIVED" CARBON SUBSTRATE FIBER SURFACE
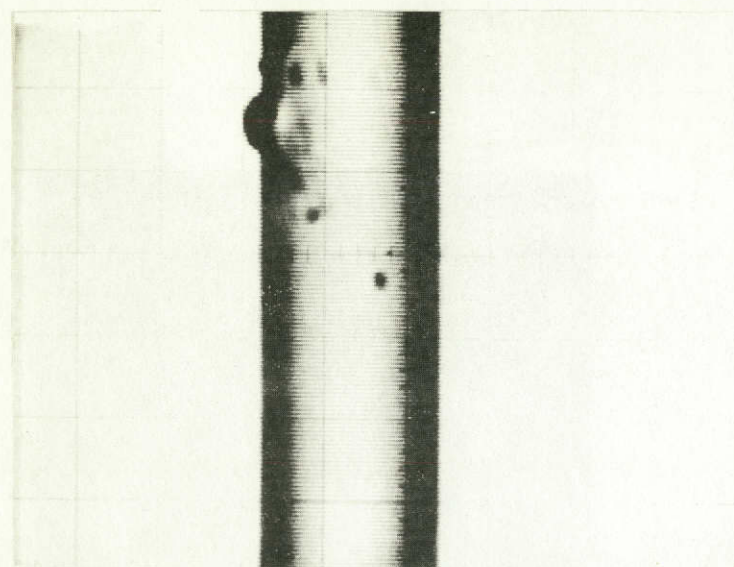
ELECTRON IMAGE 20μ
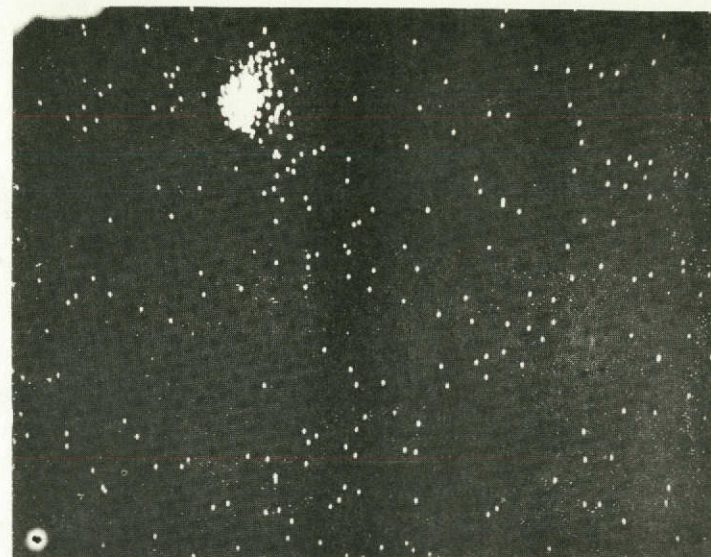
SILICON X—RAYS
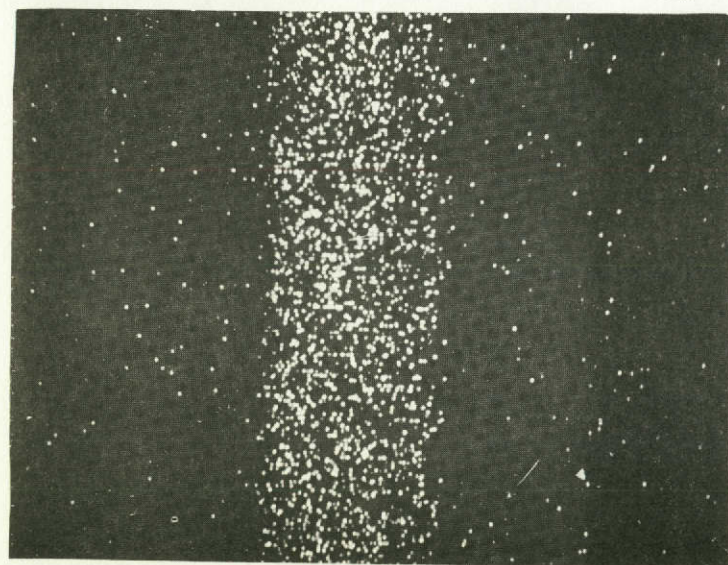
SULFUR X—RAYS

POTASSIUM X—RAYS

FIG. 6

FIG. 7
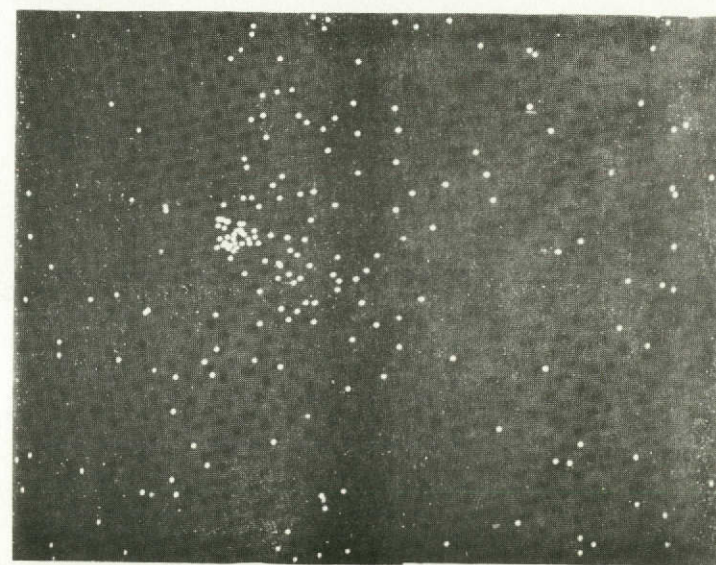
PHOTOMICROGRAPH OF A SECTION OF THE "AS RECEIVED" CARBON SUBSTRATE
FIBER AND A SECTION OF THE "AS RECEIVED" CARBON SUBSTRATE FIBER CLEANED
UNDER Cl_2 AT $1650°C$

AS RECEIVED 20μ

20μ

CLEANED UNDER Cl_2 AT $1650°C$
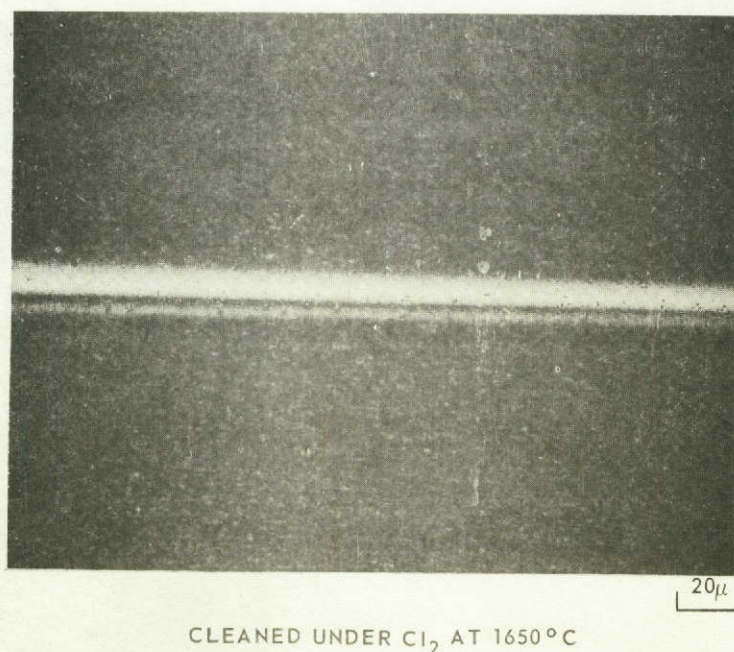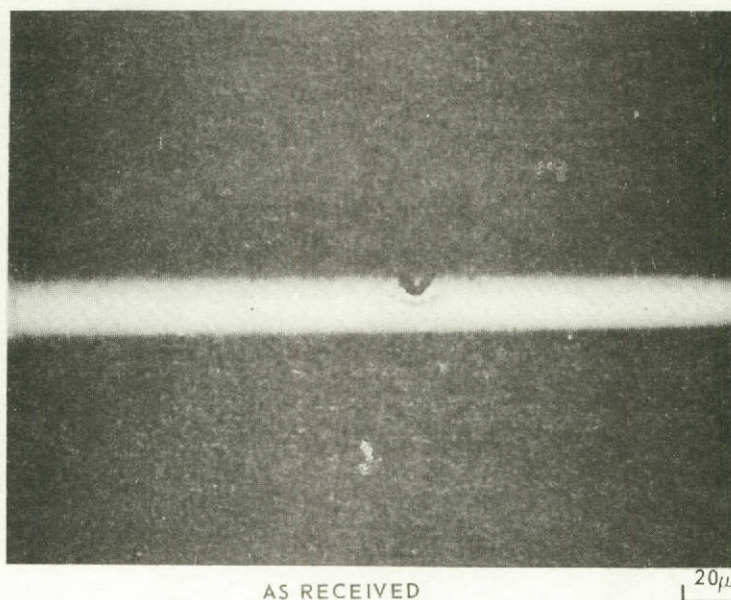
ELECTRON IMAGE AND X—RAY DISTRIBUTION PHOTOGRAPHS OF A PORTION
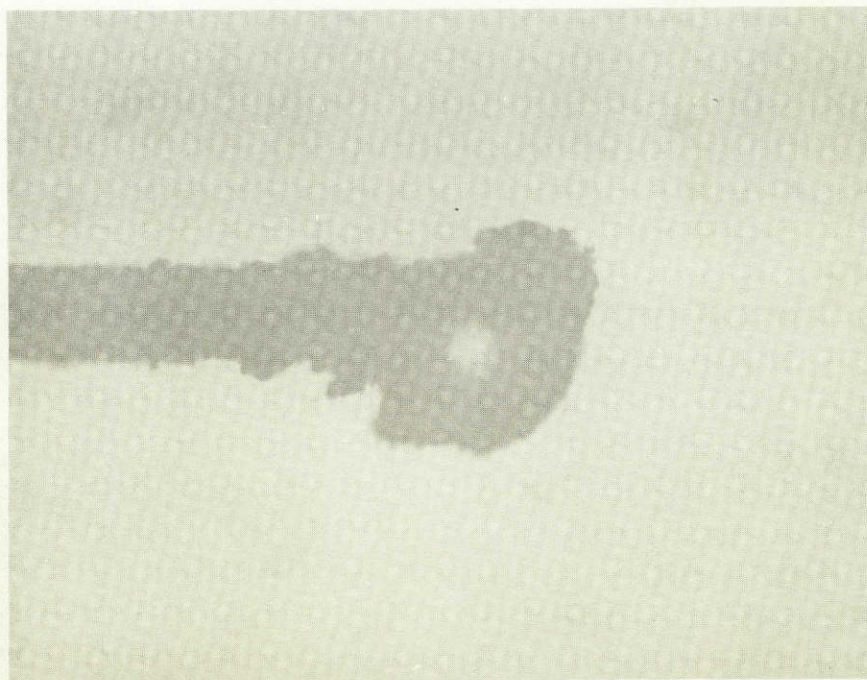OF THE FILAMENT   CLEANED IN Cl_2 AT 1650°C

ELECTRON IMAGE

10μ

CARBON X—RAYS

10μ

SULFUR X—RAYS

10μ

FIG. 8

FIG. 9
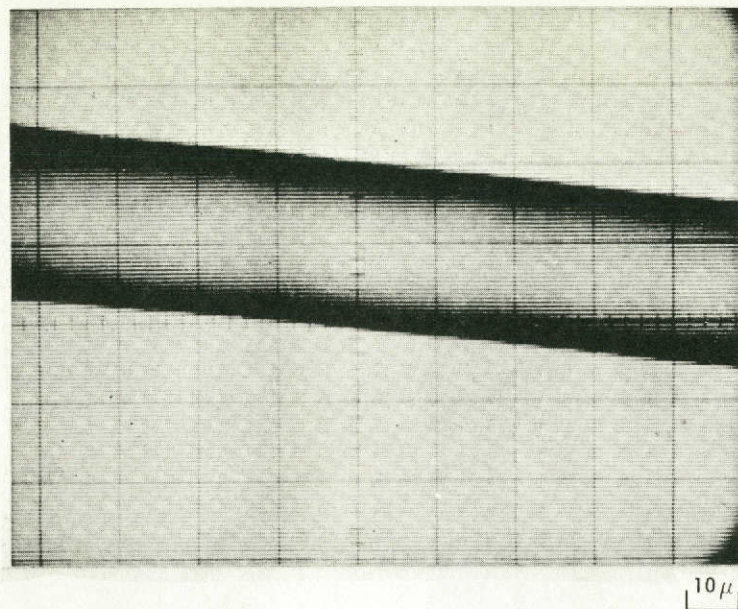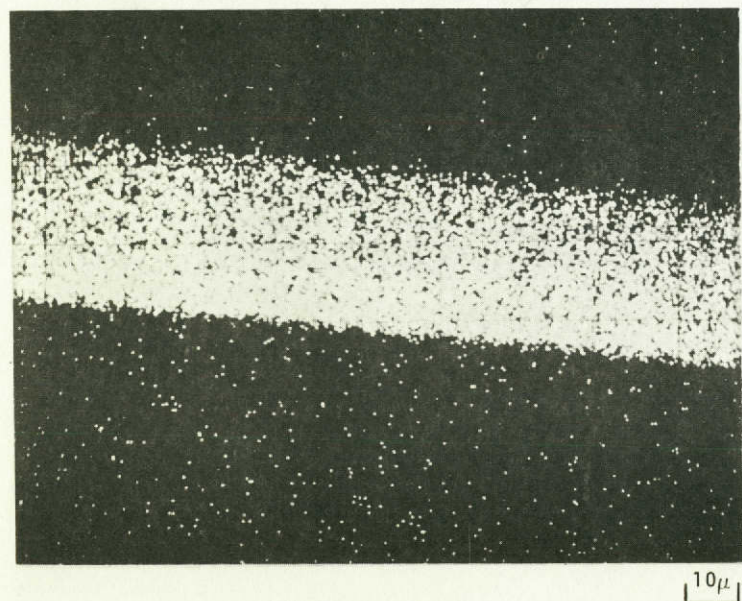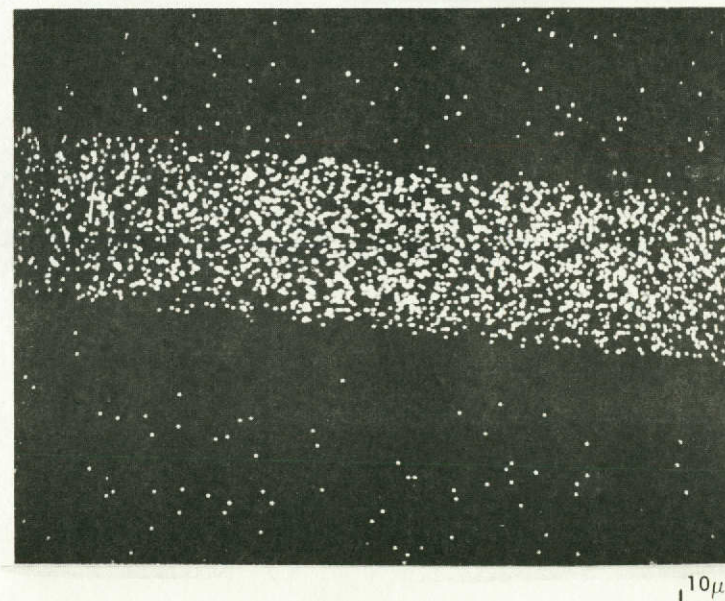
PHOTOGRAPHS OF MONOFILAMENT BREAKS
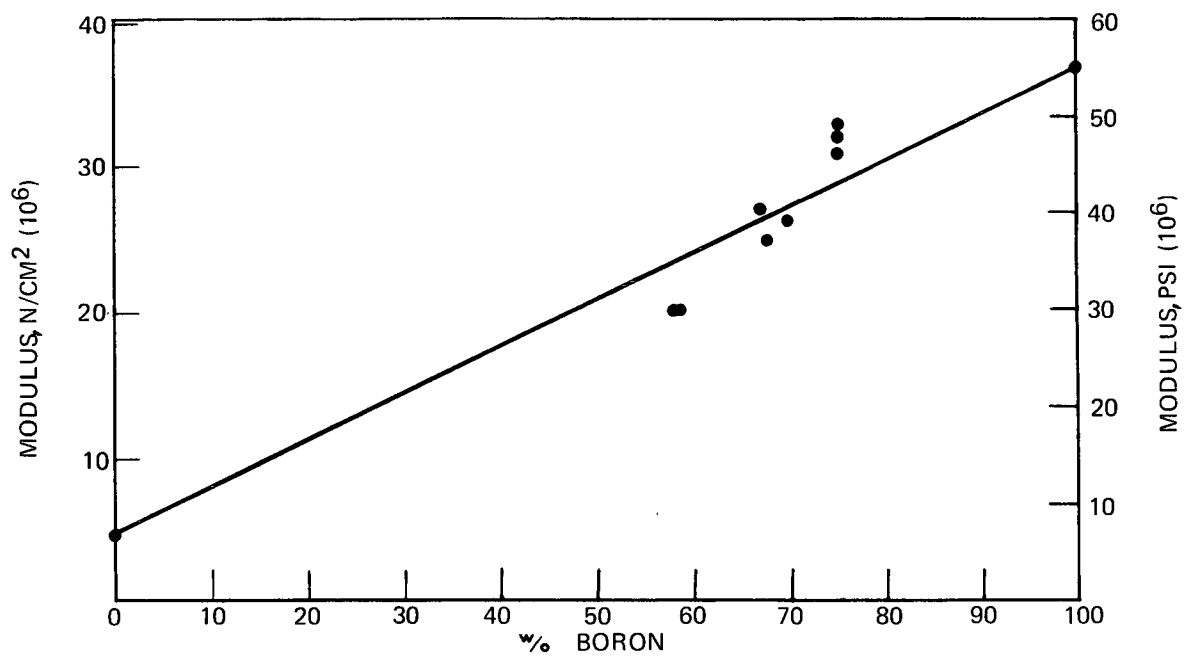THAT OCCUR WITHIN THE REACTOR
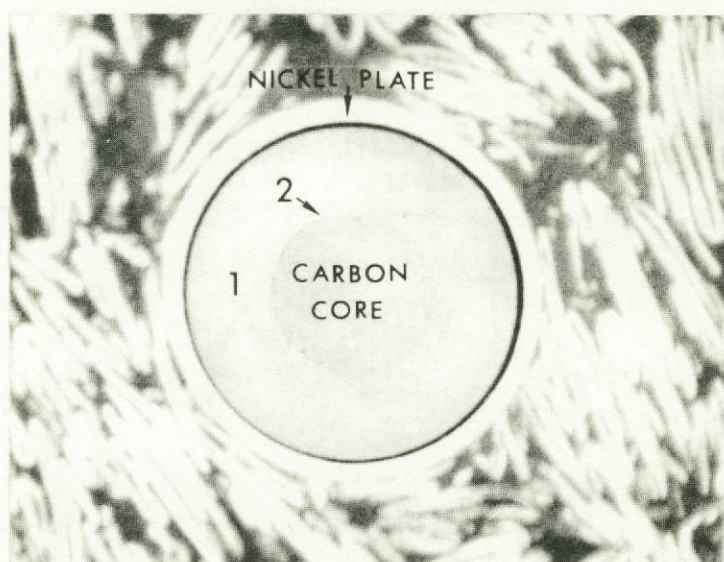

20 μ

20 μ

33

FIG. 10
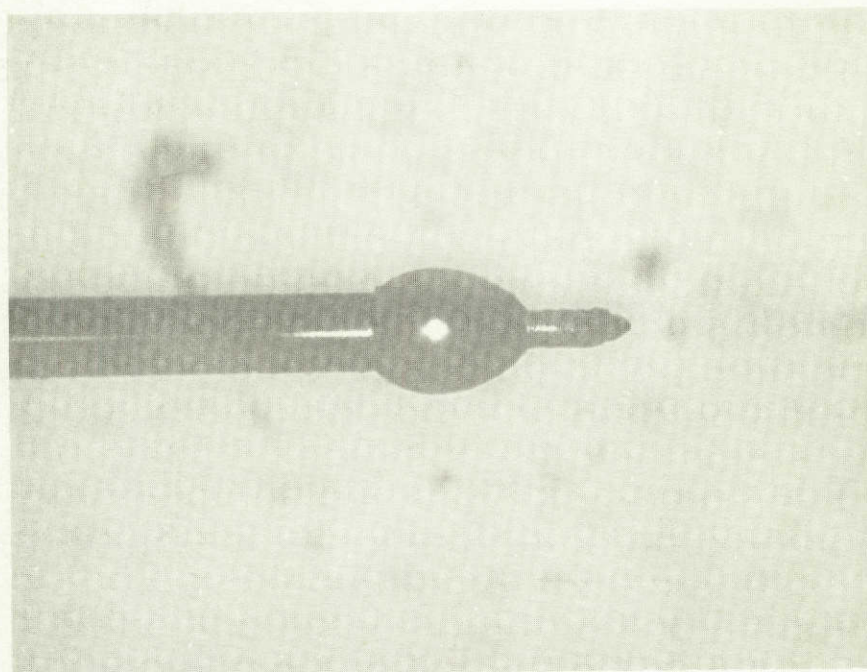
MODULUS VS w/o BORON   CARBON–BORON ALLOY MONOFILAMENT

FIG. 11

RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS,
A REPRESENTATIVE FIBER BEING SHOWN IN THIS FIGURE
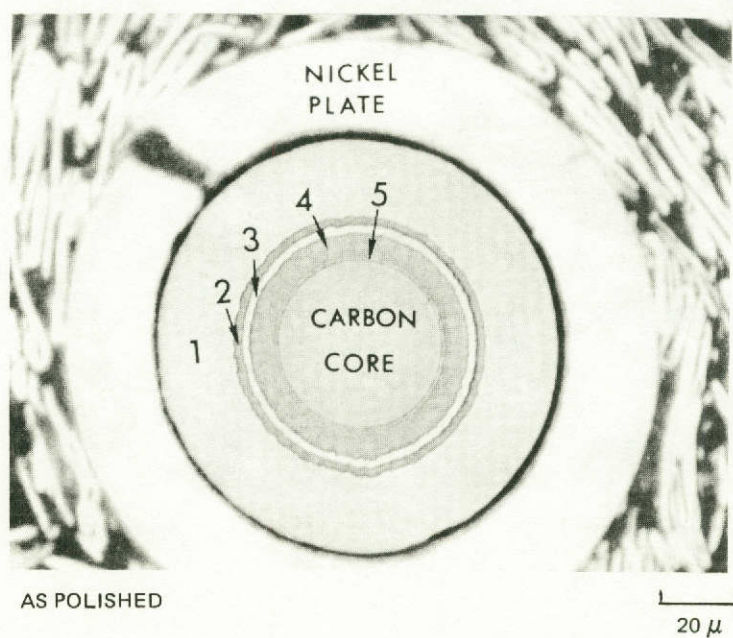
CH_4/BCl_3 RATIO = 5
POWER APPLIED = 246 WATTS

AS POLISHED

20 μ

ZONE		CONCENTRATION w/o (a/o)	
		BORON	CARBON
NO. 1	OUTER ZONE	36.8 (39.3)	63.2 (60.7)
NO. 2	INNER ZONE	32.5 (34.8)	67.5 (65.2)

FIG. 12

RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS,
## A REPRESENTATIVE FIBER BEING SHOWN IN THIS FIGURE

CH_4/BCl_3 RATIO = 5
POWER APPLIED 264 WATTS

AS POLISHED

20 μ

ZONE		CONCENTRATION w/o (a/o)	
		BORON	CARBON
NO. 1	THICK OUTER ZONE	40.0 (42.6)	60.0 (57.4)
NO. 2	DARK THIN ZONE	21.9 (23.7)	78.2 (76.3)
NO. 3	LIGHT THIN ZONE	50.2 (52.8)	49.8 (47.2)
NO. 4	DARK INNER ZONE	29.4 (31.6)	70.7 (68.4)
NO. 5	VERY THIN INNER ZONE	17.4 (19.0)	82.6 (81.0)

FIG. 13

RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS, A REPRESENTATIVE FIBER BEING SHOWN IN THIS FIGURE

CH_4/BCl_3 RATIO = 5
POWER APPLIED 300 WATTS

AS POLISHED

20 μ
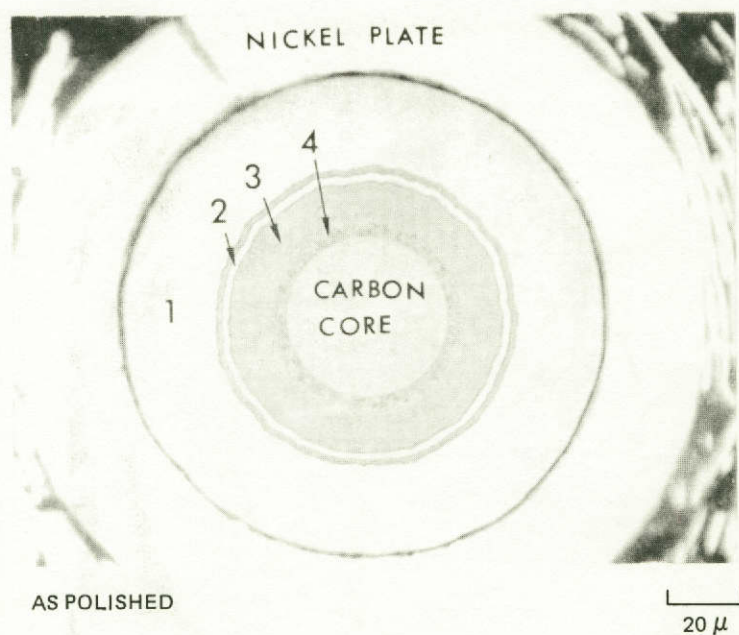
CONCENTRATION w/o (a/o)

ZONE		BORON	CARBON
NO. 1	OUTER ZONE	43.7 (46.3)	56.3 (53.7)
NO. 2	WHITE INNER ZONE	60.0 (58.2)	44.1 (41.5)
NO. 3	DARK INNER ZONE	37.6 (40.1)	62.4 (59.9)
NO. 4	VERY INNER ZONE	23.8 (25.8)	76.2 (74.3)